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Chloride in Natural Waters of New Hampshire

by

Francis R. Hall

NEW HAMPSHIRE
AGRICULTURAL EXPERIMENT STATION
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE

University of New Hampshire

PREFACE

This publication is a result of the research program of the Institute of Natural and Environmental Resources. The Institute is a multi-disciplinary group of scientists involved in a coordinated program of research, teaching, and extension. The research effort encompasses investigations of: problems affecting the quality of the environment, economics of agriculture, forest and wildlife resources, the efficient use and conservation of water and soil, and regional and community planning and development.

ACKNOWLEDGEMENTS

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The work reported herein has been accomplished as part of the research mission of the Institute of Natural and Environmental Resources at the University of New Hampshire. The research project has been supported by the New Hampshire Agricultural Experiment Station and by the United States Department of the Interior as authorized under the Water Resources Act of 1964, Public Law 88-379, through the New Hampshire Water Resource Research Center.

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SOURCE AND SIGNIFICANCE OF CHLORIDE IN NATURAL WATERS: NEW HAMPSHIRE AS A CASE HISTORY

by
Francis R. Hall [1]

INTRODUCTION

Chloride is a very mobile but chemically inactive constituent in natural waters.[2] For this reason, chloride is useful as a tracer and as an indicator of potential problems although it is not harmful to humans except at fairly high concentrations. The commonly accepted drinking water standard of 250 milligrams per liter (mg/ℓ) is basically a taste threshold, people can drink up to 1000 mg/ℓ with little difficulty. However, other elements such as sodium and heavy metals which may accompany chloride can be harmful at fairly low concentrations. Also, chloride can contribute to corrosion and vegetational kills.

Particular advantages for the study of chloride are:

1. Data for many years are likely to be available in the files of various agencies;
2. Little change in analytical techniques, so data from different times should be comparable;
3. Natural sources can generally be identified.

Chloride in the dissolved or ionized form is of major concern herein; however, the following conversion factors for the two major salt compounds referred to in the text may be of interest:

sodium chloride (weight or concentration) x (0.607) = chloride (weight or concentration)

calcium chloride (weight or concentration) x (0.639) = chloride (weight or concentration)

The concentration unit used in this report is the milligram per liter (mg/ℓ) except for solid salt where the part per million (ppm) is used. All weights are given in terms of the short ton which is equal to 2,000 pounds.

The material on which the present paper is based has come mainly from a research project entitled "Preliminary Investigation of Water Quality of New Hampshire with Emphasis on Chloride and Selected Minor Constituents". The intent herein, however, is to consider the source and significance of chloride in natural waters in a broader sense and to treat New Hampshire as a case history. The general method of approach is to consider regional aspects and to avoid individual or local problems.

[1] Professor of Hydrology, Institute of Natural and Environmental Resources, University of New Hampshire 03824

[2] J. D. HEM, STUDY AND INTERPRETATION OF THE CHEMICAL CHARACTERISTICS OF NATURAL WATERS 170-175 (U. S. Geological Survey Water-Supply Paper 1473, 2nd ed. 1970) (hereinafter cited as HEM).

SOURCES OF CHLORIDE

In order to utilize and interpret chloride data in any meaningful way, it is first necessary to establish what the normal values of chloride concentrations are naturally. These values provide a baseline for evaluating changes which may be attributed to human activity. The second thing that is needed then is to identify the activities and assess the incremental values arising from them.

NATURAL SOURCES

Potential natural sources include atmospheric precipitation, dry fallout, rock weathering, and saline water. Only the first two are of much importance to New Hampshire or to most of the northeastern United States; however, the others can be of considerable importance elsewhere.

Atmospheric Precipitation and Dry Fallout

The quantitative importance of chloride from atmospheric precipitation and dry fallout varies with climate and distance from the ocean. For example, considerable chloride in surface waters comes from the ocean in the southeastern and northeastern parts of the United States[2a, 3] whereas only a small amount does in the southwestern U.S.[4] With the ocean as a major source, lines of equal chloride concentration (isochlors) can be expected to approximately parallel and decrease inland from the ocean. This type of trend is shown in Figure 1 where concentrations are about 10 mg/ℓ near the ocean and drop to less than one inland. A comparable picture for Massachusetts is given in Motts and Saines[5] and for all of New England and New York in Jackson.[6]

A difficult question to answer is the amount of chloride which is dissolved in atmospheric precipitation and the amount which occurs as dry fallout during precipitation-free periods or is washed out of the atmosphere during precipitation. Even if chloride in rain and snow is mainly recycled sea salt this need not be the case for dry fallout which can include material extracted from dust

[2a] A. W. GAMBELL & D. W. FISHER, CHEMICAL COMPOSITION OF RAINFALL, EASTERN NORTH CAROLINA AND SOUTHEASTERN VIRGINIA K9 (U.S. Geological Survey Water-Supply Paper 1535-K, 1966).

[3] F. J. PEARSON, JR. & D. W. FISHER, CHEMICAL COMPOSITION OF ATMOSPHERIC PRECIPITATION IN THE NORTHEASTERN UNITED STATES P5-P8 (U.S. Geological Survey Water-Supply Paper 1535-P, 1971).

[4] HEM 171.

[5] W. S. MOTTS & M. SAINES, THE OCCURRENCE AND CHARACTERISTICS OF GROUND-WATER CONTAMINATION IN MASSACHUSETTS FIGURE 2 (University of Massachusetts, Water Resources Research Center 7, 1969).

[6] D. D. JACKSON, THE NORMAL DISTRIBUTION OF CHLORINE IN THE NATURAL WATERS OF NEW YORK AND NEW ENGLAND PLATE 10 (U.S. Geological Survey Water-Supply Paper 144, 1905). (hereinafter cited as JACKSON).

picked up by the wind. Juang and Johnson[7] present data showing that part of the chloride leaving a small watershed in northern New England likely comes from dry fallout. Based on Figure 1, Jackson[8], Juang[9] and Pearson and Fisher,[10] the author believes 0.5 mg/ℓ is a reasonable estimate for average chloride reaching land surface in New Hampshire.

Igneous, Metamorphic and Sedimentary Rocks

Few rocks with the exception of evaporites are likely to contain much chloride within their structures.[11] Evaporite deposits are derived by evaporation of sea and lake water usually in closed basins. Marine evaporites in particular are likely to be extensive and high in chloride. Therefore, water associated with these rocks will also be high. For example, the Pecos River receives a considerable increment of chloride from evaporites in southeastern New Mexico.[12] A consideration of regional geology should show whether evaporites are likely to be present in any particular area. For example, they are not present in New England.

Concentrations in sedimentary, igneous and metamorphic rocks range from 15 mg/ℓ for sandstone up to 300 or more for shale.[13] Rock dissolution or weathering will produce only very small concentrations in surface or ground water although over time the accumulation may be large. Metamorphic rock weathering is only a minor source in one small watershed in New Hampshire.[14] Chloride entrapped in sedimentary rocks leaving or entering after deposition can be a significant item, and this will be discussed in the section on saline water.

Saline Water

Saline water may either be entrapped in sedimentary rocks during deposition or may enter later. The former is probably most common in sandstone and shale whereas the latter may occur in almost any rock near saline water. Two good examples are brines found associated with petroleum deposits and sea-water propagated inland by tides. The question of presence of brines is best answered

[7] Juang & Johnson, *Cycling of Chlorine through a Forested Watershed in New England*, 72 J. Geophysical Research 5641-5647 (1967). (hereinafter cited as Juang).

[8] JACKSON.

[9] Juang.

[10] F. J. PEARSON, JR. & D. W. FISHER, CHEMICAL COMPOSITION OF ATMOSPHERIC PRECIPITATION IN THE NORTHEASTERN UNITED STATES (U.S. Geological Survey Water-Supply Paper 1535-P, 1971).

[11] Johns & Huang, *Distribution of chlorine in terrestrial rocks*, 31 Geochimica et Cosmochimica Acta 35-49 (1967).

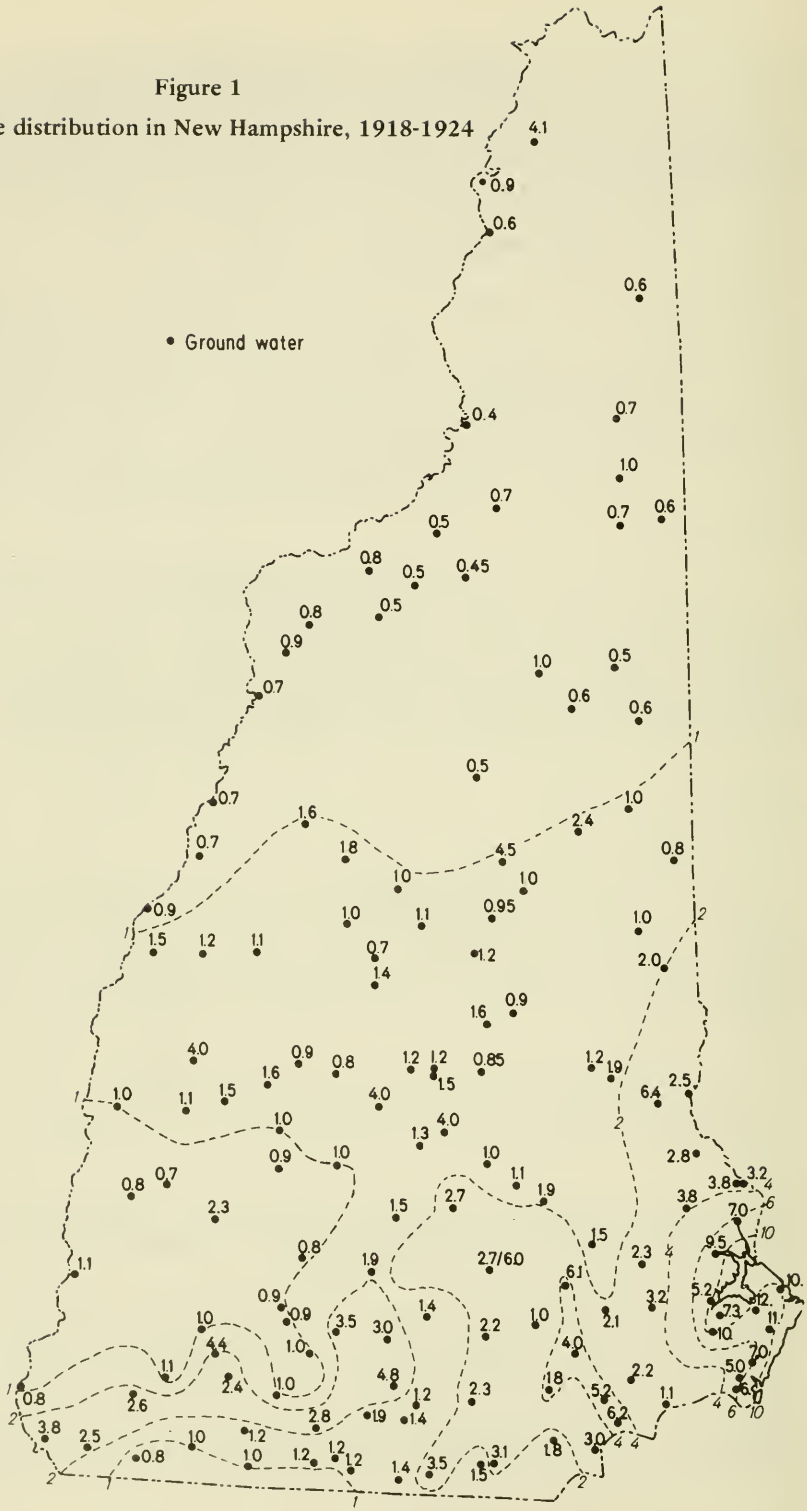
[12] HEM 174.

[13] Id. 171.

[14] Juang.

Figure 1

Chloride distribution in New Hampshire, 1918-1924



by a consideration of regional geology. For example, brines are not likely to be found in New England, but chloride from sea water is found in streams and ground-water reservoirs or aquifers near the coast. Unless extensive intrusion is caused by human activities such as excavations or ground-water removal, the latter is significant only in a fairly narrow coastal strip.

Saline water in sedimentary rocks may also emerge in springs at the surface of the earth. Depending on original depth, such water may be warm or hot. Also, springs associated with volcanoes or recent volcanic activity may contain chloride. It is beyond the scope of this paper to discuss whether this chloride actually comes from the depths of the earth or is recycled sea salt. As with the cases discussed above, the likely presence of such sources is best determined from geological considerations.

SOURCES ASSOCIATED WITH MAN

The Minerals Yearbook for 1971[15] gives the following breakdown of salt used in the United States in 1970: road deicing salt — 23 percent; food and food-related uses — 17 percent; water softeners — 5.6 percent; and all other uses, mainly industrial — 54.4 percent. A detailed source-by-source discussion would become lengthy and confusing, so the approach will be to aggregate sources into major categories of sewage and septic tank effluents, industrial effluents, and road deicing salt. The sources associated with man are more homogeneous in distribution than are the natural sources, hence they are as important in New Hampshire as elsewhere.

Ordinary Sewage and Septic Tank Effluents

Contributions of chloride from human wastes undoubtedly vary with climatic and other factors, but a reasonable value is that each human being contributes about five to nine grams of chloride in excreta per day[16,17] which is equivalent to four to seven pounds per capita per year. Kitchen and normal commercial and manufacturing wastes contribute on the order of 14 pounds per capita per year, and this combines with the human excreta value for a rule-of-thumb value of 20 pounds per capita per year contribution of chloride from these sources.[18] In general, the chloride level in effluents is raised some 40 to 80 mg/ℓ over the basic value in the effluent-bearing water.

[15] I. U.S. BUREAU OF MINES, MINERALS YEARBOOK, 1971, METALS, MINERALS, AND FUELS 1031-1041 (1973).

[16] C. N. SAWYER & P. L. McCARTY, CHEMISTRY FOR SANITARY ENGINEERS 378 (2nd ed. 1967).

[17] G. M. FAIR, J. C. GEYER, & M. C. MORRIS, WATER SUPPLY AND WASTE WATER DISPOSAL 549 (1954).

[18] O'Connor & Mueller, *A water quality model of chlorides in Great Lakes*, Proceedings American Society of Civil Engineers 96, No. SA4, 955-975, 1970.

Water softeners that are charged with sodium chloride may also be a source of chloride particularly in areas of hard water. This is not much of a problem in New Hampshire, but in places where the water is hard a chloride increase of perhaps 100 mg/ℓ has been suggested.[19] This could be as much as 25 pounds per capita per year in addition to the 20 pounds given above.

Industrial Effluents

The widespread variations in the location and concentration of industries such as chemical plants or oil refineries where effluents may be high in chloride makes difficult any form of generalizations as to assignment of rule-of-thumb values. For example, Lakes Huron, Michigan, and Ontario receive several million tons per year from chemical plants and similar industries.[20] New Hampshire appears to have no area where really high concentrations of chloride can be attributed to industries although there are individual point sources. So the combined 20 pounds per capita per year figure is assumed adequate to include all industries on a state-wide basis.

Road Deicing Salt

The increasing use of sodium chloride and calcium chloride as road deicing salt has caused serious concern as evidence accumulates for its contamination of water, corrosion of automobiles, and vegetational kills.[21],[22] The major usage has been since the mid 1940's with sodium chloride being by far the more heavily used compound. However, both chloride salts were used earlier for deicing on roads, and calcium chloride has also been used to hold down dust. Direct contamination of ground and surface waters has occurred due to inadequately designed and maintained storage piles of salt.

The amount of road salt applied is a function of both climate and philosophy on "bare" highways. State highway departments in the eastern and northeastern United States use between 20 and 40 tons of salt per lane mile per year with most states using 30 tons or less.[23] States in the southern and western parts of the United States use only minor amounts or no road deicing salt. Specific data

[19] E. J. STRUZESKI, JR., ENVIRONMENTAL IMPACT OF HIGHWAY DEICING 47 (U.S. Environmental Protection Agency, Water Pollution Control Research Series, 11040 GKK 06/71, 1971). (hereinafter cited as STRUZESKI).

[20] O'Conner & Mueller, *A water quality model of chlorides in Great Lakes,* Proceeding, American Society of Civil Engineers 96, No. SA4, 955-975, 1970.

[21] R. FIELD, E. J. STRUZESKI, JR., H.E.M. MASTERS, & A. N. TAFURI, WATER POLLUTION AND ASSOCIATED EFFECTS FROM STREET SALTING 34 (U.S. Environmental Protection Agency, National Environmental Research Center, EPA R2-73-257, 1973). (hereinafter cited as FIELD).

[22] R. C. TERRY, JR., ROAD SALT, DRINKING WATER, AND SAFETY – IMPROVING PUBLIC POLICY AND PRACTICES 64-65 (1974). (hereinafter cited as TERRY).

are given for many states in sources such as Terry,[24] Struzeski,[25] Field,[26] Highway Research Board,[27] Hanes,[28] and Hawkins?[29] Unfortunately, most of these sources focus on state highway departments and similar large agencies while giving little attention to how much road deicing salt is used by county and municipal agencies. Terry[30] does indicate that in 1969, road salt use by 25 Greater Boston communities was about 47,000 tons.

New Hampshire was an early user of road deicing salt, and on a highway mileage basis it has also been a fairly heavy user. By 1966-1967 estimated cumulated use was 2,300,000 tons.[31] In the early to mid 1960's, the annual use on state highways was about 85,000 tons, but in the later 1960's and early 1970's the figure was 150,000 tons. Then both by decision and by benefit of a mild winter or two the figure has dropped to 100,000 tons of salt in recent years. Based on limited data the present author estimates that towns and cities probably use at least 33,000 tons of sodium chloride per year.

Miscellaneous

One possible source of chloride already alluded to is saline water intrusion due to pumpage of ground water or similar activities by man. This is most commonly thought of as occurring near the ocean, but it can occur any place where saline water bodies are present. High chloride values due to this are likely to be fairly localized. In New Hampshire, intrusion is occurring around Great Bay and the nearby Atlantic Ocean, and, although important locally, it is of minor importance regionally.

The fairly common assumption that dissolved natural chlorine gas or chlorine gas used in water treatment or other processes can be a source of chloride is not correct. Without going into detail, the oxidation state of chlorine is so high that dissociation to chloride is not likely under ordinary conditions at the earth's surface;[32] hence, chlorine is not a likely source of chloride in natural waters.

[23] STRUZESKI 18-19.

[24] TERRY.

[25] STRUZESKI.

[26] FIELD.

[27] ENVIRONMENTAL DEGRADATION BY DE-ICING CHEMICAL AND EFFECTIVE COUNTER-MEASURES (Highway Research Board Record 425, 1973).

[28] R. E. HANES, L. W. ZELAZNY, & R. E. BLASER, EFFECTS OF DEICING SALTS ON WATER QUALITY AND BIOTA-LITERATURE REVIEW AND RECOMMENDED RESEARCH (Highway Research Board, National Cooperative Highway Research Program Report 91, 1970).

[29] PROCEEDINGS STREET SALTING – URBAN WATER QUALITY WORKSHOP AT STATE UNIVERSITY COLLEGE OF FORESTRY, SYRACUSE UNIVERSITY (R. H. Hawkins ed., 1971).

[30] TERRY 81.

[31] STRUZESKI 18.

[32] HEM 170-171.

CHLORIDE IN NEW HAMPSHIRE

A useful way to illustrate what can be done with chloride information is to make approximate chloride balances for New Hampshire at two different times, 1920 and 1970, and to consider what happened during the intervening period. Additional insights may be obtained from examples of chloride change in surface water and ground water.

STATEWIDE BALANCE, 1920

It is assumed for purposes of this paper that Figure 1 gives a reasonable picture of "natural" chloride distribution in New Hampshire and that 1920 is a reasonable year for a "natural" chloride balance. True natural distribution of chloride in the state probably can never be determined because New Hampshire has been settled for a long time, and data are available for only a short, recent period. Nevertheless, human activities are not likely to have had much influence except locally before the Civil War or even later. Where the data exist, a town by town comparison shows little or no change between data given by Jackson[33] at the turn of the century and the 1918-1924 data collected for the present study.

By 1918, however, there is definite evidence for unusually high chloride in some drinking water, mainly from wells. The likely source of chloride is probably a cesspool or perhaps in a few cases calcium chloride for dust control. Such high values were not used in preparation of Figure 1, but the possibility still exists that some of the higher values on the map particularly in the southern part of the state reflect human influences. Where possible, data used on Figure 1 are from municipal or industrial supplies and from public institutions. To fill in gaps, however, data from private, usually home supplies, are used. Also, only ground-water data are used where possible. In a few cases lakes are used, but not streams.

The approximate chloride balance for 1920 is given in Table 1. The balance is based on the simple assumption that annual inflow equals annual outflow plus or minus a change in storage. The implicit assumption is made that the residence time of chloride and water is one year, and that the system is in a more or less steady state condition so that the change in storage is negligible. These assumptions pose few problems for 1920 except for a possible slight increase in storage occurring due to human influence.

The precipitation and runoff figures are statewide averages given by McGuinness.[34] The difference between precipitation and runoff of 20 inches represents the loss of water by evaporation and use of water by vegetation. As this is about 50 percent, chloride concentration in rainfall can be expected to double after reaching the earth's surface. Therefore, if average chloride in 1920 in the waters of the state was one mg/ℓ then chloride in precipitation should

[33] JACKSON 15-18.

[34] MCGUINNESS, THE ROLE OF GROUND WATER IN THE NATIONAL WATER SITUATION 524 (U.S. Geological Survey Water-Supply Paper 1800, 1963).

have been about 0.5 mg/ℓ. The 20 lb. per capita chloride figure for humans is used although it may be a little large.

The outflow total of 18,900 tons or concentration of 1.2 mg/ℓ is the consequence of the assumptions used in the balance. An examination of published data up to 1920 suggests this is quite reasonable as shown by the area weighted mean of 1.3 mg/ℓ in Table 2.

Table 1.

Chloride Balance for New Hampshire, 1920

Inflow		Chloride, Tons
Atmospheric Precipitation and Dry Fallout[1]		14,500
Human Activity[2]		4,400
	Total	18,900
Outflow		
Surface water and Ground water[3]		18,900
Change in Storage[4]		0

1. 0.5 mg/ℓ chloride in 43 inches of precipitation on 9,300 square miles.
2. 20 lbs. per capita per year for 443,000 people.
3. Equivalent to 1.2 mg/ℓ chloride in 23 inches of runoff from 9,300 square miles.
4. Assumed zero, but human activities may actually be sufficient to cause a small increase in storage.

Table 2.

Drainage for New Hampshire Areas, Average Runoff, Chloride Tonnage and Concentrations for New Hampshire

Drainage Basin	Area, miles²[1]	Area %	Annual Runoff, Inches	1920 Tons	Chloride mg/ℓ	1970 Tons	Chloride mg/ℓ
Androscoggin	743	8.0	24.26[2]	1,050	.8[4]	6,540	5[7]
Saco	862	9.3	31.91[2]	1,800	.9[4]	7,980	4[6]
Connecticut	3,058	32.9	21.95[2]	4,380	.9[5]	38,900	8[8]
Merrimack	3,770	40.6	22.46[2]	9,210	1.5[5]	73,700	12[8]
Piscataqua	848	9.1	21.00[3]	3,870	3.0[6]	9,040	7[9]
Total	9,281	99.9		20,310		136,160	
Area weighted mean			23.16		1.3		8.7

1. LAND, WATER, RECREATION – THE WATER RESOURCES OF NEW HAMPSHIRE 117 (New Hampshire State Planning Project Report No. 10, 1965).

2. WATER RESOURCES DATA FOR MASSACHUSETTS, NEW HAMPSHIRE, RHODE ISLAND, AND VERMONT, 1972, (U.S. Geological Survey, 1974).

3. Estimated from data in Id.

4. F. W. CLARKE, THE COMPOSITION OF THE RIVER AND LAKE WATERS OF THE UNITED STATES 24 (U.S. Geological Survey Professional Paper 135, 1924).

5. M. D. Leighton, NORMAL AND POLLUTED WATER IN NORTHEASTERN UNITED STATES 37-38 (U.S. Geological Survey Water-Supply Paper 79, 1903).

6. Estimated by author.

7. Estimated from data in WATER RESOURCES DATA FOR MAINE, 1972, (U.S. Geological Survey, 1973) and records in UNH files.

8. Discharge weighted value approximated from data in WATER RESOURCES DATA FOR MASSACHUSETTS, NEW HAMPSHIRE, RHODE ISLAND, AND VERMONT, 1971, (U.S. Geological Survey, 1973).

9. Based on Lamprey River and Oyster River data in UNH files.

STATEWIDE BALANCE, 1970

The general chloride distribution for 1968-1970 in New Hampshire is given in Figure 2. These data are taken where possible from municipal water supplies utilizing ground water. However, private well supplies and in a few cases municipal ponds or lakes are used to fill in the gaps. Except for municipal supplies an attempt was made to avoid wells contaminated with road deicing salt. The intent is to show the overall picture without emphasizing local problems such as wells close to highways. Some of the values near the coast may reflect saline-water intrusion.

The approximate chloride balance for 1970 is given in Table 3. Here the general steady-state assumption is not so bad for water, but problems do occur for chloride. For example, a large water body such as Lake Winnipesaukee or groundwater in an extensive glacial deposit may have a residence time of a number of years. Therefore, chloride content to some extent is a function of what happened in prior years.

Put another way, if road deicing salt is either increased or decreased one year the resulting effect will not necessarily occur entirely in the same year or even the next year.

In 1971, 103,000 tons of chloride (equivalent to 169,000 tons of sodium chloride) were shipped into New Hampshire.[35] Similar data are not available for 1970. This compares favorably with the 118,000 tons calculated for 1970 for human activities and road deicing salt in Table 3.

CHANGES FROM 1920 to 1970

A comparison of Figures 1 and 2, Tables 1 and 3, or the 1920 and 1970 chloride columns in Table 2 gives a general picture of what happened from a period of reduced human activity to recent times. The increases in chloride concentrations may not seem large, but they do represent substantial increases in storage. An even clearer picture is given in Figures 3 through 9 which are scatter diagrams of chloride plotted against time for seven municipal water supplies. The locations are shown on Figure 2. These examples were selected to cover the state geographically. They are from ground-water supplies except Laconia which represents outflow from Lake Winnipesaukee.

Chloride is plotted for convenience on a logarithmic scale on Figures 3 through 9, but there is no necessary implication that chloride is actually increasing logarithmically over extended periods of time. Therefore, any attempt at projections beyond final data points in 1970 should be done with extreme caution. Also, the data points are from all samples sent into the State laboratory, and it is not possible to follow any one source except Laconia with time. Some

[35] I U.S. BUREAU OF MINES, MINERAL YEARBOOK, 1971, METALS, MINERALS, AND FUELS 1031-1041 (1973).

Figure 2

Chloride Distribution in New Hampshire, 1968-1970

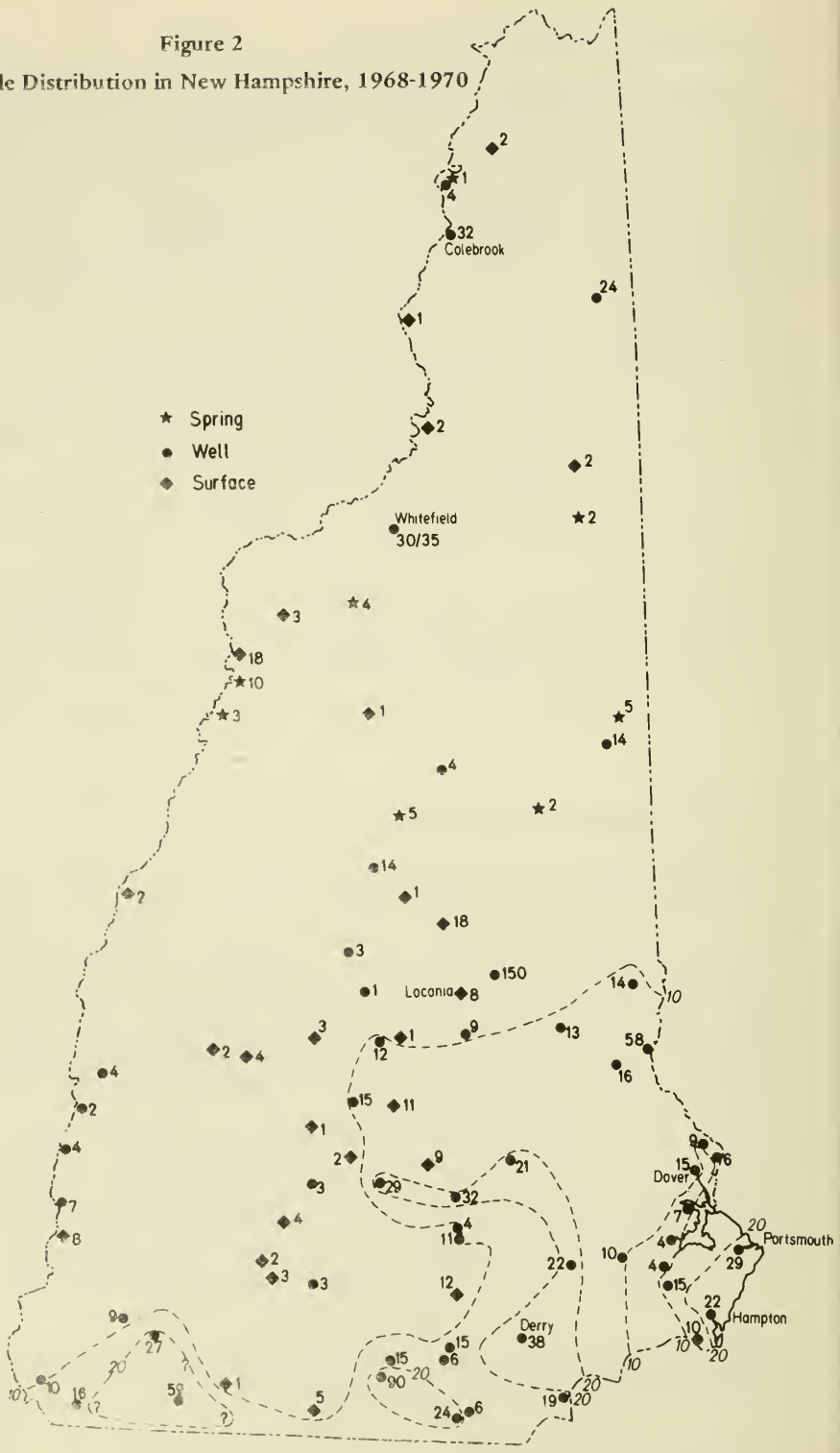


Table 3.

Chloride Balance for New Hampshire, 1970

Inflow	Chloride, Tons
Atmospheric Precipitation and Dry Fallout[1/]	14,500
Human Activity[2/]	7,400
Highway Deicing Salt[3/]	91,000
Town Road Deicing Salt[4/]	20,000
	132,900
Outflow	
Surface and Groundwater[5/]	135,900
Change in Storage[6/]	−3,000

1. 0.5 mg/ℓ chloride in 43 inches of precipitation on 9,300 square miles.
2. 20 pounds per capita for 738,000 people.
3. 150,000 tons sodium chloride. Approximate average for period leading into 1970.
4. Estimate based on assumed 33,000 tons sodium chloride.
5. Calculated from area weighted mean of 8.7 mg/ℓ from Table 2 in 23 inches of runoff from 9,300 square miles.
6. There more likely is an increase in storage, but this factor is not easy to evaluate because of uncertainties in the balance.

unusually high values in the early part of the record and unusually high or low values later on cannot be explained with any confidence.

Particular points of interest in Figures 3 through 9 can be summarized as follows:

1. There is slight evidence at best for increasing chloride between 1918 and 1945.
2. After 1945 chloride increases in all of the supplies. This essentially coincides with the beginning of increased road deicing salt applications.
3. Only one place (Figure 5) has chloride in a well approaching or beyond the accepted standard of 250 mg/ℓ. Nevertheless overall increases range from about two-fold (Figure 6) to about eighty-fold (Figure 3).
4. Some of the supplies such as Laconia (Figure 7) appear to be starting to level off by 1970. This would suggest that input and output has essentially reached steady state at a new and higher chloride level.
5. None of the supplies appear to show any decline. However, such declines may occur as road deicing salt applications have been decreased since 1972.
6. The 1920 and earlier average chloride concentration for Lake Winnipesaukee is 1.2 mg/ℓ and the 1970 figure is 9 mg/ℓ. The difference between these may not seem impressive but it does represent an addition of some 28,000 tons of chloride to storage.

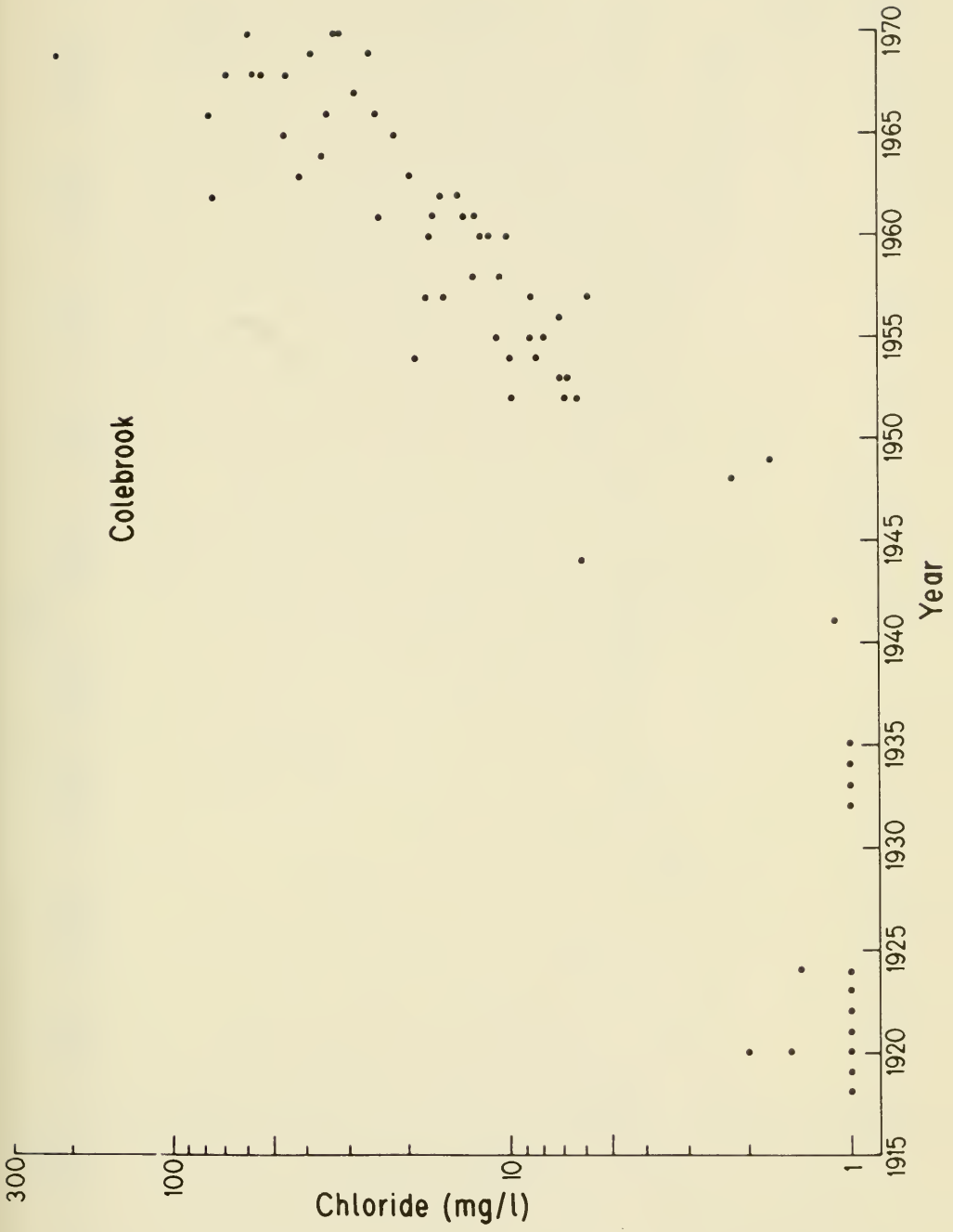


Figure 3

Chloride for 1918-1970 at Colebrook Groundwater Supply

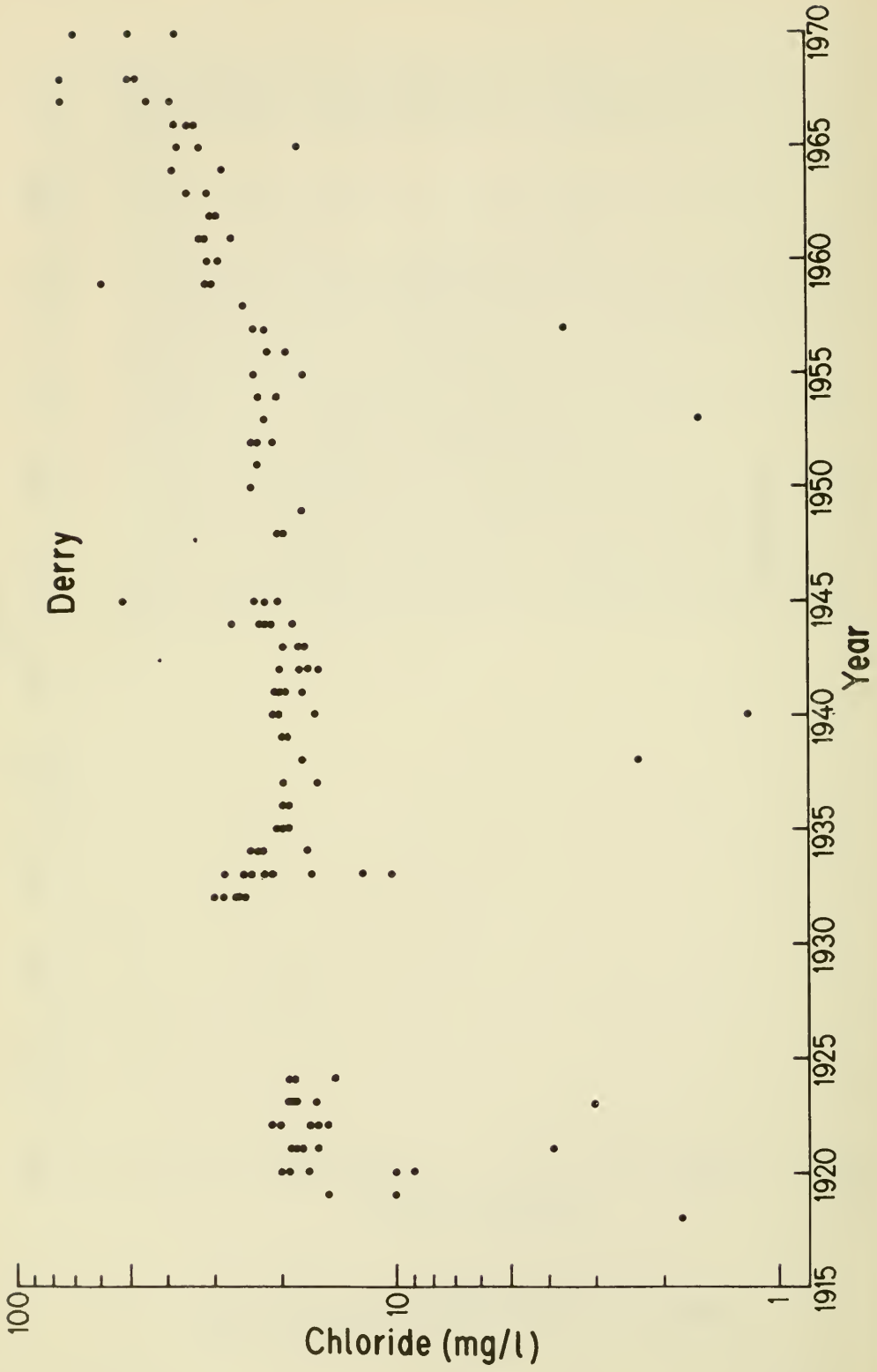


Figure 4

Chloride for 1918-1970 at Derry Groundwater Supply

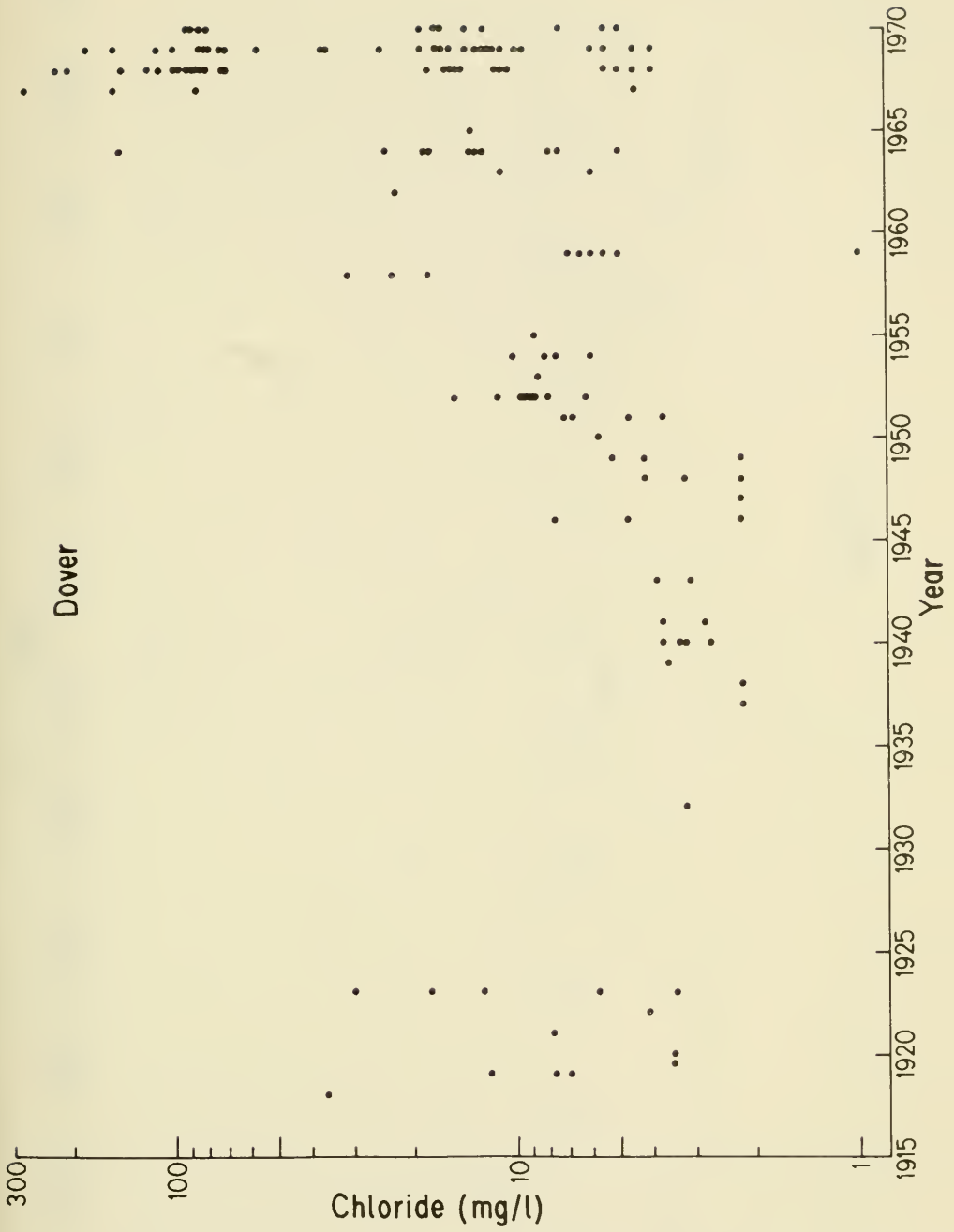


Figure 5

Chloride for 1918-1970 at Dover Groundwater Supply

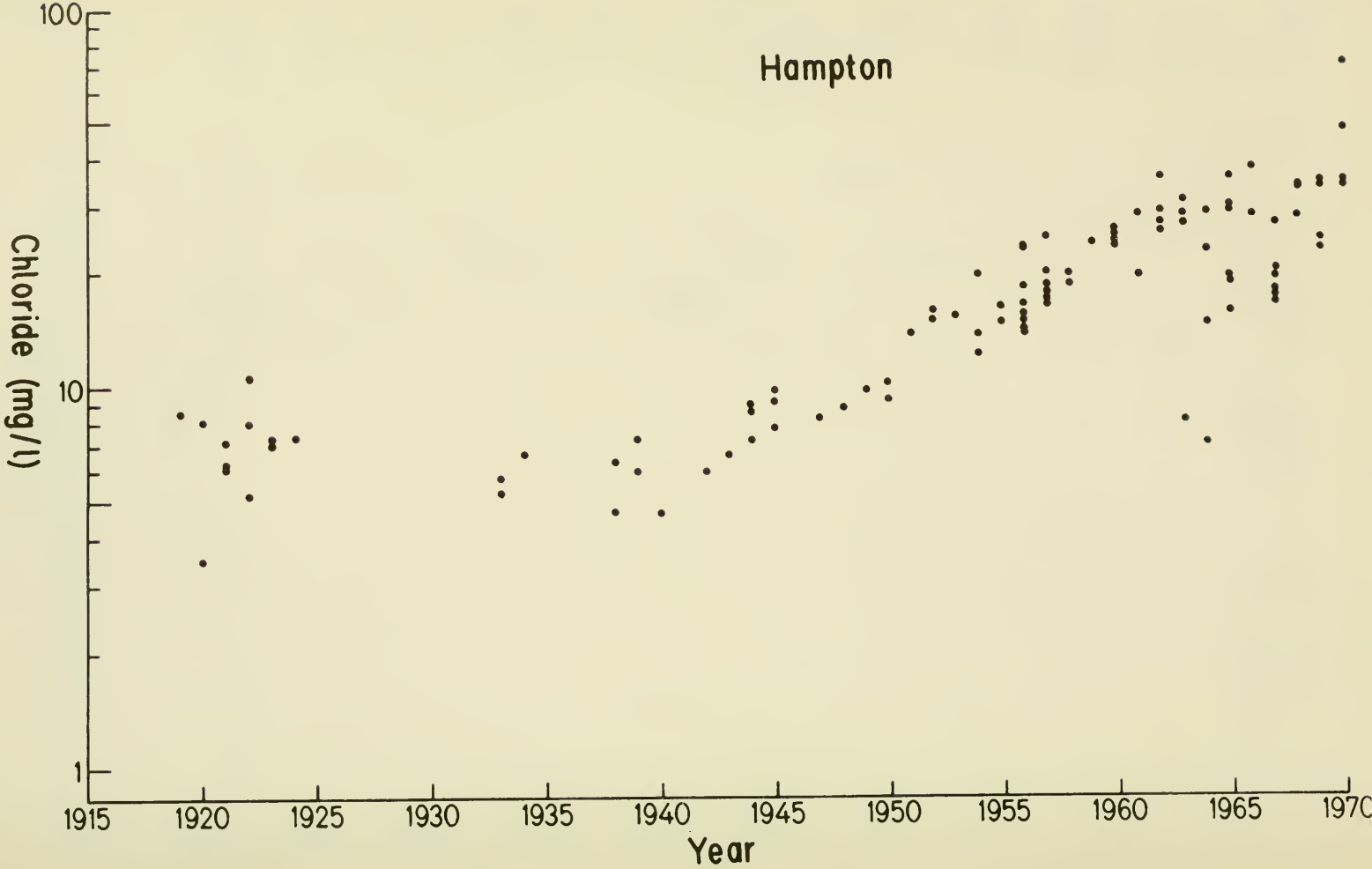


Figure 6
Chloride for 1918-1970 at Hampton Groundwater Supply

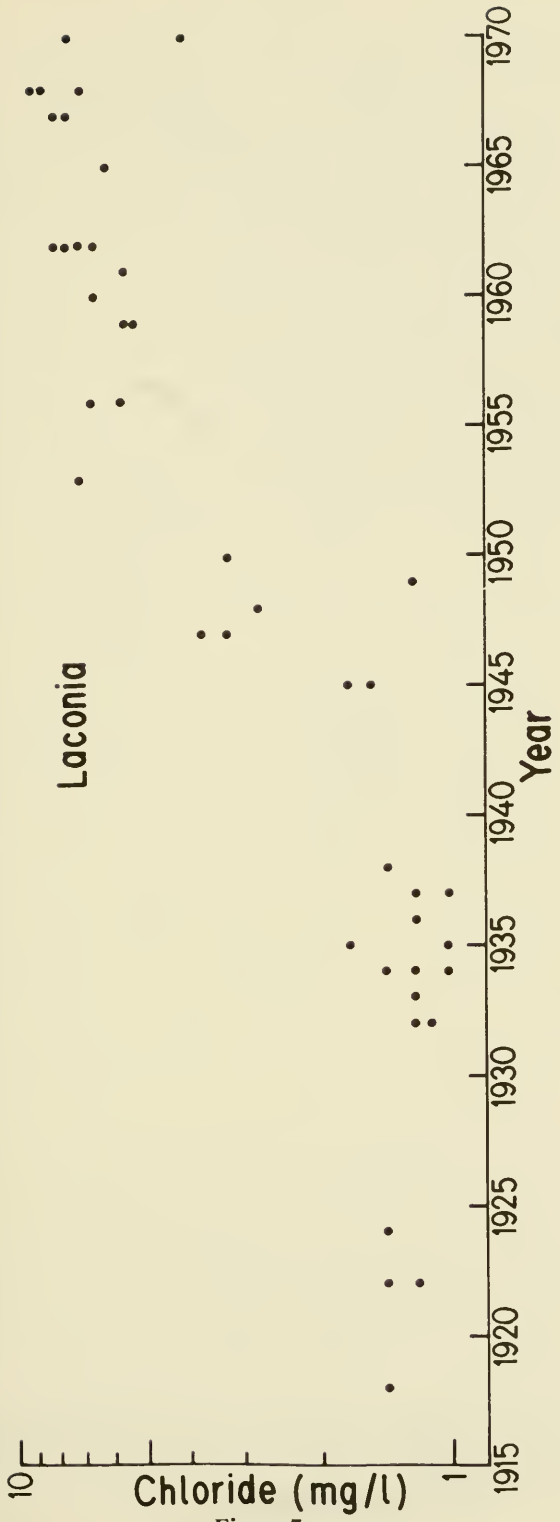


Figure 7

Chloride for 1918-1970 at Laconia Surface Water Supply

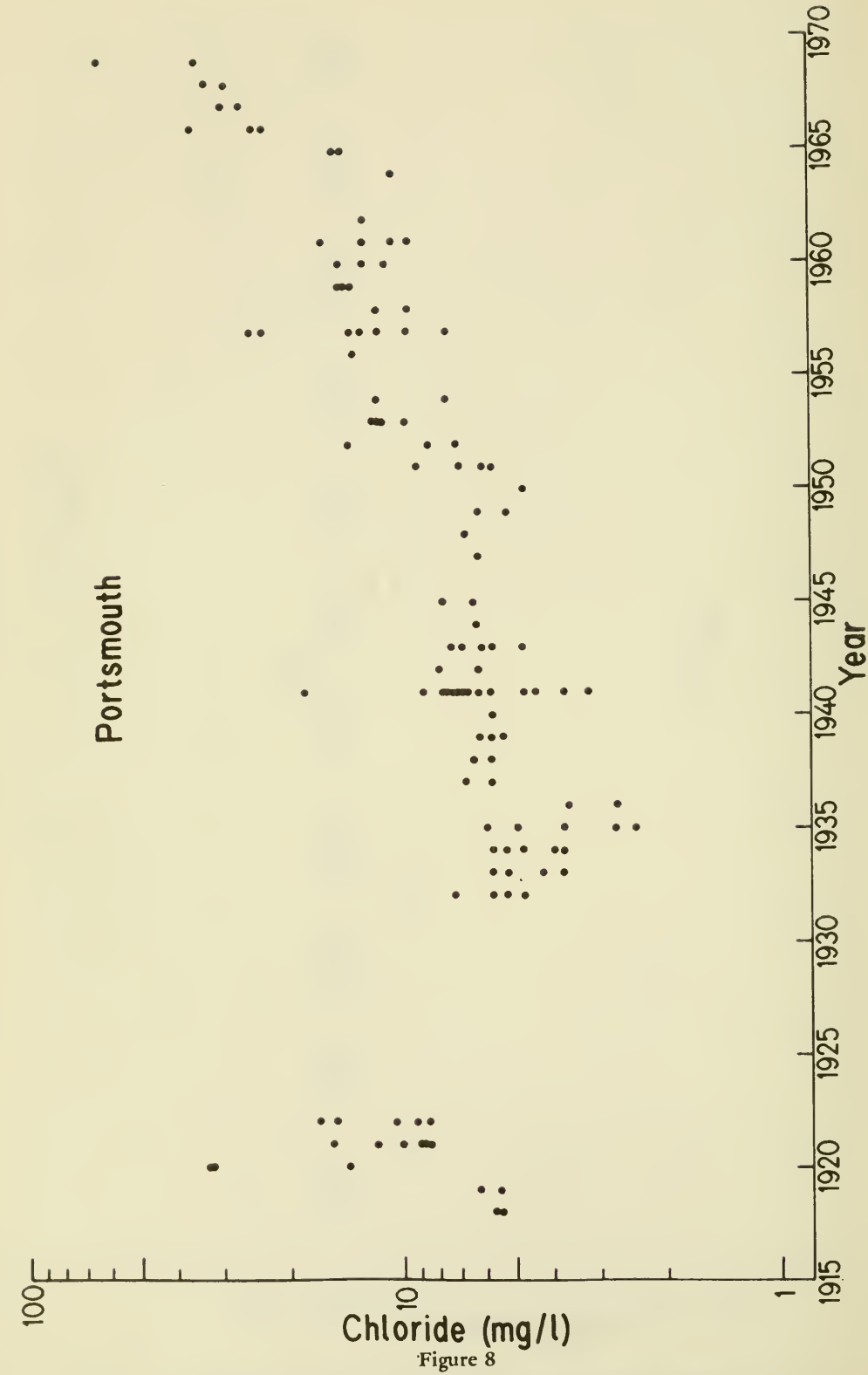


Figure 8

 Chloride for 1918-1970 at Portsmouth Groundwater Supply

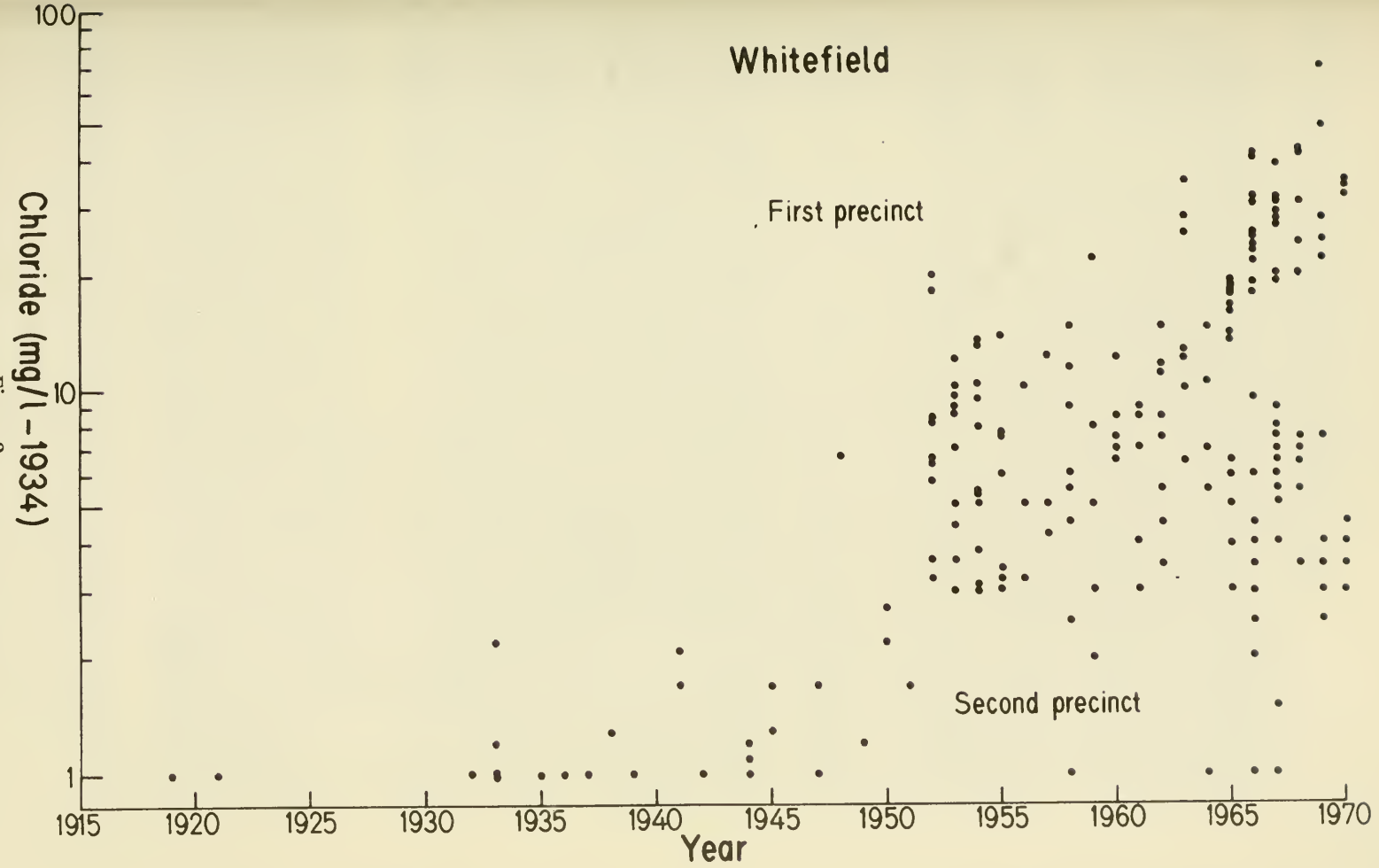


Figure 9

Chloride for 1918-1970 at Whitefield Groundwater Supply

WHAT DOES IT ALL MEAN?

A general picture has been presented as to how chloride in New Hampshire has increased from more or less natural concentrations to present levels. On a statewide basis, the increase in discharge has been about seven fold, and the increase in storage has been at least two fold. The importance of road deicing salt is obvious. However, nothing in the general picture seems to indicate any severe problems with chloride. Nevertheless, as suggested by Figures 3 through 9, problems have arisen and can be expected to continue. Therefore, the general picture needs to be modified by taking a closer look at certain aspects.

One important feature is that the chloride increase has come mainly in the more urbanized areas and along highways, whereas mountainous areas above highways have been little effected. Attention should be centered on more localized areas and to the indirect effects as alluded to in the introduction. These are discussed briefly by major topic rather than in a detailed fashion. Emphasis is placed on material not adequately covered in the literature.

VEGETATION AND SOILS

The effect of road deicing salt on vegetation and soils was seen fairly early in New England[36,37] and elsewhere.[38] Vegetation with low salt tolerance such as various species of maples, elms, and grasses are killed or seriously impaired within about 30 feet of salted highways. Sodium is the major source of trouble although chloride may be at higher concentrations. The killing or damaging of vegetation not only has aesthetic implications, but practical ones as well because vegetation serves to control erosion and shrubbery and trees muffle traffic sounds.

Sodium affects soils by causing an alteration to a less desirable structure. The sodium from road deicing salt or other source of chloride, replaces or exchanges for calcium and magnesium, thereby impairing fertility and permeability.[39] An interesting side effect is that ground and surface waters may show more increase in calcium and magnesium than in sodium. Chloride is not likely to replace other anions in soils, but it may become delayed in transit due to the depletion of soil moisture above the water table.[40] This chloride will be flushed downward when adequate soil water moves through the soil.

[36] Lacasse & Rich, *Maple Decline in New Hampshire*, 54 Phytopathology 1071-1075 (1964).

[37] Hutchinson, *Environmental Pollution from Highway Deicing Compounds*, 25 J. Soil and Water Conservation 144-146 (1970).

[38] STRUZESKI 85-96.

[39] Id, 86

[40] Toler & Pollack, *Retention of chloride in the unsaturated zone*, 2 J. Research U.S. Geological Survey 119-123 (1974).

NATURAL WATERS

Data already given in the tables, Figure 7, and the text show how chloride buildup occurs in large rivers and one large lake. A potential problem is that small streams and ponds or partially closed bays, may reach much higher chloride levels which can impair biologic activity or even prevent an annual overturn.[41] Figures 3 through 6 and 8 through 9 show buildup in various groundwater reservoirs or aquifers, but little can be added because of the absence of information about physical properties, volume, and residence times. Some useful insights can be obtained, however, by consideration of what might be expected as shown by a mathematical model for dispersion from a highway.

Computer simulations of a modified form of a model developed at Colorado State University[42] have been performed at the University of New Hampshire for thin, narrow acquifers overlying bedrock. The results show that chloride will build up and fluctuate seasonally close to a highway. This has been observed from measurements in many wells and concentrations may reach 1000 mg/ℓ chloride or more. Away from the highway, however, the model indicates that lower but more or less steady state values will prevail once chloride outflow to a nearby water body equals inflow from the highway. This has not been commonly observed because most monitoring programs emphasize wells close to highways. This steady state situation should occur after a few years of application of salt, and the chloride should flush out a few years after cessation of salting.

The implication is that in small, thin aquifers intersected by streams such as are commonly found in much of New England, buildup of chloride may not be a serious problem except close to highways. Chloride from septic tanks may act in much the same way but for the special case of a point source. This optimistic view must be tempered somewhat, however, by the fact that ecologic problems from increased chloride may develop in ponds, streams, and wetlands draining the aquifers. This aspect does not seem to have received much attention.

If the same computer model is applied to larger aquifers such as for the supplies shown in Figures 3 through 6 and 8 through 9, then the same general pattern develops except buildup away from the highway will likely be greater. Also, the aquifer will flush much more slowly because of volume and if salting ceases the impact of chloride is more serious than in the thinner aquifers.

CORROSION

The corrosion associated with road deicing salt of automobile bodies, concrete pavement and structures, metal manhole covers and so on, is discussed well in the literature[43,44] but the potential toxicity of the corrosion products

[41] PROCEEDINGS, STREET SALTING – URBAN WATER QUALITY WORKSHOP AT STATE UNIVERSITY COLLEGE OF FORESTRY, SYRACUSE UNIVERSITY 74-79 (R. H. Hawkins ed, 1971)

[42] D. L. REDDELL & D. K. SUNADA, NUMERICAL SIMULATION OF DISPERSION IN GROUNDWATER AQUIFERS (Colorado State University Hydrology Papers 41, 1970).

[43] FIELD 34.

[44] STRUZESKI 77-80.

has not been as thoroughly covered. A few years ago, the author suggested that some heavy metals such as hexavalent chromium, which is toxic to humans, might be released by corrosion of car bodies and move into surface and groundwaters. Little progress has been made in evaluating the validity of this idea, but preliminary field studies indicate that corrosion of home water systems is potentially a serious problem. Although corrosion occurs mainly by oxidation, the process is enhanced in the presence of solutions containing chloride.[45]

A typical home-water system involves pumping from a stone or concrete lined dug well or drilled well with steel casing, through a plastic or iron pipe, to a dwelling where flow is into copper tubing through an iron pressure tank, back into copper tubing. Iron and copper and impurities may be released, and, in addition, zinc and cadmium may be released if galvanized piping is involved. In a state such as New Hampshire where groundwater tends to be in the pH 5.5-7.5 range, the end result can be considerable corrosion of copper as well as other metals, thereby causing deterioration of the water system and posing a health hazard. Added chloride can only make the problem worse.

A sampling for chemical analysis including iron, zinc, copper, lead, and hexavalent chromium of a pond, a stream, and 18 wells along U.S. 4, from Great Bay four miles east of Durham, to Northwood Ridge 15 miles west of Durham, was undertaken in the summer of 1972. The results must be treated carefully because of the small number of samples, lack of knowledge about the water systems, and problem of determining in some cases, whether chloride was from road deicing salt or a septic tank. Also, with the exception of iron, which is more unsightly than a health hazard, all values are lower than accepted standards.

Nevertheless, one domestic well close to the highway had water with 174 mg/ℓ of chloride, a pH of 6.0, and 0.395 mg/ℓ hexavalent chromium which is uncomfortably high. There is a definite tendency in the samples for high chloride to be associated with low pH and fairly high zinc and copper. Lead levels are low and appear to represent natural background. Iron ranges from 0.09 mg/ℓ to 19 mg/ℓ, but relationships to chloride are not obvious. An interesting point is that during the study, many people complained about corrosion of their own water system or remarked on similar problems of others. Clearly, additional work needs to be done to assess what is happening and to pose corrective measures for both economic and health reasons.

ELEMENTS ACCOMPANYING CHLORIDE

Apart from the chloride itself, the accompanying constituents may produce problems. Considerable emphasis has recently been placed on sodium which is the other major component of most road deicing salt.[46] Several aspects have already been discussed in the section on vegetation and soils. Also, there has been considerable controversy over whether or not hard (high in calcium and magnesium) or soft (high in sodium and low in calcium and magnesium) drinking waters have implications for health. A hard water can have considerable sodium

[45] Id.

[46] TERRY 38-41.

(seawater for example), whereas soft water cannot have much calcium or magnesium; so these terms should be used correctly and cautiously.

The matter of hard water versus soft water is left to others, but Terry[47] has reviewed and summarized known health hazards from sodium ingestion for cardio-vascular, kidney, and liver ailments with emphasis on essential hypertension which requires severe limitations of sodium. Problems also arise with some complications in pregnancy and with some metabolic disorders. For healthy people, 270 mg/ℓ sodium is a reasonable upper limit in drinking water, whereas, 20 mg/ℓ is the upper limit for those suffering form hypertension.[48] Certainly then, there is cause for concern with any buildup in chloride even if some sodium is exchanged for calcium and magnesium.

Salt for table use, deicing, water softeners, and so on, is usually nearly pure sodium chloride whether from evaporated or rock salt. Nevertheless, minor constituents may pose problems. For example, a Chilean rock salt analyzed by the New Hampshire Water Supply and Pollution Control Commission contained 64 parts per million (ppm) zinc and six ppm orthophosphate. Fresh-water fish have a low tolerance for zinc, and phosphate can contribute to eutrophication of ponds and lakes.

Another aspect of some concern has been possible effects of deicing additives (anti-caking) such as ferric ferrocyanide (Prussian blue) and sodium ferrocyanide and corrosion inhibitors such as certain chromates (apparently no longer used) and sodium hexametaphosphate.[49] The ferrocyanides, particularly in the sodium form, are somewhat soluble in water, and cyanide is harmful even in low concentrations to some aquatic life. Hexavalent chromium is toxic to humans, and trivalent chromium is toxic to some vegetation.

IMPLICATIONS FOR THE FUTURE

Rather than the traditional summary and conclusions, I prefer to close on a more personal note. Clearly, mankind is going to continue using salts containing chloride for a variety of purposes. Very likely, use of road deicing salt will continue, but recent events suggest a trend toward much closer control of quantity and better methods of application. Perhaps substitutes will be found. The hard water versus soft water controversy will continue, and maybe it will turn out to hinge on some as yet undetected trace element. Pollution problems will not go away, and there will always be combined indifference and hand wringing.

We do live on a large but finite planet which is not likely to possess infinite capacity to absorb at rapid rates the wastes and by-products resulting from man's activities. It is essential that apparently harmless constituents such as chloride be given consideration at the same time as more harmful substances. In closing, I would point to the reaction against nonbiodegradable detergents which caused water from wells to foam. In response, producers developed a biodegradable detergent that does not cause foaming; however, its products may still be there. We just do not see them any longer. Chloride should be viewed in the same light. It has something to tell us.

[47] Id.

[48] TERRY 41-43.

[49] STRUZESKI 65-70.

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